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PHYS 362 HW 12

Problem 1

a.) $G = E - TS + PV$: $dG = dE - dT \cdot S - T \cdot dS + dP \cdot V + P \cdot dV$

$dE = TdS - PdV$ $\quad dG = \cancel{TdS} - \cancel{PdV} - SdT - T\cancel{dS} + VdP + \cancel{PdV}$

$dG = -S \cdot dT + V \cdot dP$

$$dG = VdP - SdT$$

$$dG = \left(\frac{\partial G}{\partial P}\right)_V dP + \left(\frac{\partial G}{\partial T}\right)_S dT \qquad \left(\frac{\partial G}{\partial P}\right)_V dP + \left(\frac{\partial G}{\partial T}\right)_S dT = VdP - SdT$$

$$\boxed{\begin{gathered} dG = VdP - SdT \\ V = \left(\frac{\partial G}{\partial P}\right)_V , \quad S = -\left(\frac{\partial G}{\partial T}\right)_P \end{gathered}}$$

b.) $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \qquad \frac{\partial^2 G}{\partial P \partial T} = \frac{\partial^2 G}{\partial T \partial P}$

$$\frac{\partial^2 G}{\partial P \partial T} = -\left(\frac{\partial S}{\partial P}\right)_T : \frac{\partial^2 G}{\partial T \partial P} = \left(\frac{\partial V}{\partial T}\right)_P \quad \therefore \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial P}\right)_P$$

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial P}\right)_P}$$

Problem 2

a.) $H = E + PV$: $dH = dE + PdV + dPV$

$$= TdS - \cancel{PdV} + \mu dN + \cancel{PdV} + VdP$$

$$= TdS + \mu dN + VdP$$

$$dH = TdS + \mu dN + VdP$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP$$

$$\left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP = TdS + \mu dN + VdP$$

$$\boxed{T = \left(\frac{\partial H}{\partial S}\right)_{P,N},\ \mu = \left(\frac{\partial H}{\partial N}\right)_{S,P},\ V = \left(\frac{\partial H}{\partial P}\right)_{S,N}}$$

b.) $\left(\frac{\partial T}{\partial P}\right)_{S,N} = \frac{\partial^2 H}{\partial P \partial S}$: $\left(\frac{\partial V}{\partial S}\right)_{P,N} = \frac{\partial^2 H}{\partial S \partial P}$: $\frac{\partial^2 H}{\partial P \partial S} = \frac{\partial^2 H}{\partial S \partial P}$

$\therefore \left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}$

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}}$$

Problem 3

a.) $H = E + PV \quad : \quad dH = dE + Pdv + vdP$

$$= Tds - P\cancel{dv} + P\cancel{dv} + vdP$$

$$dH = Tds + vdP$$

$$ds = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \quad : \quad dH = T\left(\cancel{\left(\frac{\partial S}{\partial T}\right)_P}^{\,0} dT + \left(\frac{\partial S}{\partial P}\right)_T dP\right) + vdP$$

$$dH = T\left(\frac{\partial S}{\partial P}\right)_T dP + vdP \quad : \quad \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V}$$

b.) $\left(\frac{\partial H}{\partial P}\right)_T = 0 \quad : \quad \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V \quad : \quad \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \quad : \quad PV = NkT$

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -T\left(\frac{Nk}{P}\right) + V = -\frac{NkT}{P} + \frac{NkT}{P} = 0 \quad \checkmark$$

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_T = 0}$$

Problem 4

a.) $C_V = \left(\frac{\partial E}{\partial T}\right)_V$, $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$: $\left(\frac{\partial C_V}{\partial V}\right)_T = T\frac{\partial^2 P}{\partial T^2}$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial^2 E}{\partial V \partial T}\right) : \left(\frac{\partial^2 E}{\partial T \partial V}\right) = \cancel{\left(\frac{\partial P}{\partial T}\right)_V} + T\left(\frac{\partial^2 P}{\partial T^2}\right) - \cancel{\left(\frac{\partial P}{\partial T}\right)_V} = T\left(\frac{\partial^2 P}{\partial T^2}\right)$$

$$\boxed{\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)}$$

b.) $\left(\frac{\partial E}{\partial V}\right)_T = \frac{N^2 a}{V^2}$, $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$: $E = \frac{3}{2}NkT - \frac{N^2 a}{V}$: $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

$$\left(\frac{\partial E}{\partial V}\right)_T = \frac{d}{dV}\left(-\frac{N^2 a}{V}\right) = \frac{N^2 a}{V^2} \quad \therefore \quad \left(\frac{\partial E}{\partial V}\right)_T = \frac{N^2 a}{V^2} = C_V$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\frac{\partial^2 P}{\partial T^2} : \left(P + \frac{N^2}{V^2}a\right)(V - Nb) = NkT : PV - PNb + \frac{N^2 a}{V} - \frac{N^3 ab}{V^2} = NkT$$

$$P(V - Nb) = \frac{N^3 ab}{V^2} - \frac{N^2 a}{V} + NkT : P = \frac{1}{(V-Nb)}\left(\frac{N^3 ab}{V^2} - \frac{N^2 a}{V} + NkT\right)$$

$$\frac{\partial P}{\partial T} = \frac{Nk}{(V-Nb)} : \frac{\partial^2 P}{\partial T^2} = 0 : \left(\frac{\partial C_V}{\partial V}\right)_T = T \cdot 0 = 0$$

$$\boxed{\left(\frac{\partial E}{\partial V}\right)_T = \frac{N^2 a}{V^2}, \left(\frac{\partial C_V}{\partial V}\right)_T = 0}$$

c.) $\left(\frac{\partial E}{\partial T}\right)_V = C_V$, $f'(V) = \frac{N^2 a}{V^2}$

$$\int dE = C_V \int dT : E = C_V \Delta T + f(V)$$

$$\int f(V) = N^2 a \int V^{-2}\, dV \quad f(V) = -\frac{N^2 a}{V}\Big|_{V_i}^{V_f} = -N^2 a\left(\frac{1}{V_f} - \frac{1}{V_i}\right) = N^2 a\left(\frac{1}{V_i} - \frac{1}{V_f}\right)$$

$$\boxed{E(V,T) = C_V \Delta T + N^2 a\left(\frac{1}{V_i} - \frac{1}{V_f}\right)}$$

Problem 5

$T = 298\ K$, $P = 1.01 \times 10^5\ Pa$, $C_p = 73\ J/mol\,K$, $\alpha = 207 \times 10^{-6}\ K^{-1}$, $K = 3.57 \times 10^{-10}\ Pa^{-1}$

$\rho_{H_2O} = 1000 \frac{kg}{m^3}$, $\rho_{H_2O} = 18 \frac{g}{mol}$ $\therefore$ $m = 0.018\ kg$: $\rho = \frac{m}{V}$ $\therefore$ $V = \frac{m}{\rho} = \frac{0.018\ kg}{1000\ kg/m^3} = 1.8 \times 10^{-5}\ m^3$

$V = 1.8 \times 10^{-5}\ m^3$

$C_p = C_v + TV\frac{\alpha^2}{K}$ $\therefore$ $C_v = C_p - T \cdot V \cdot \frac{\alpha^2}{K} = 73 \frac{J}{mol\ K} - (298\ K)(1.8 \times 10^{-5}\ m^3) \frac{(207 \times 10^{-6}\ K^{-1})^2}{(3.57 \times 10^{-10}\ Pa^{-1})} = 72.4 \frac{J}{mol\ K}$

$$\boxed{C_v = 72.4 \frac{J}{mol\ K}, \quad C_p \approx C_v \ \text{Not much diff}}$$